

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION
SPONSORED PROJECT INITIATION

Date: October 1, 1979

Project Title: New Functional Groups and Hypervalent Molecules

Project No: G-33-643 *Green card*

Project Director: Dr. Edward M. Burgess

Sponsor: National Science Foundation

Agreement Period: From 10/1/79 Until 3/31/83 (Grant Period)

Type Agreement: Grant No. CHE-7900923, dtd. August 17, 1979

Amount: \$26,143 NSF (G-33-643)
1,257 GIT (G-33-351)
\$27,400 Total

Reports Required: Annual Progress Report (w/request for continued support); Final Project Report

Sponsor Contact Person (s):

Technical Matters

NSF Program Officer
R. S. Macomber, Synthetic Organic Program
Chemical Synthesis and Analysis Section
Division of Chemistry
Directorate for Mathematics and Physical
Sciences and Engineering
National Science Foundation
Washington, D. C. 20550
202/634-4381

Contractual Matters

(thru OCA)
NSF Grants Official
Martin V. Geary
MPE/STIA Branch, Section I
Division of Grants and Contracts
Directorate for Administration
National Science Foundation
Washington, D. C. 20550
202/632-5900

Defense Priority Rating: N/A

Assigned to: Chemistry (School/Laboratory)

COPIES TO:

Project Director
Division Chief (EES)
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Library, Technical Reports Section
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EES Reports & Procedures
Project File (OCA)
Project Code (GTRI)
Other _____

SPONSORED PROJECT TERMINATION/CLOSEOUT SHEET

Date 11/11/83

Project No. G-33-643 School/~~OSU~~ Chemistry

Includes Subproject No.(s) N/A

Project Director(s) Dr. Edward M. Burgess GTRI / ~~GRI~~

Sponsor National Science Foundation

Title "New Functional Groups and Hypervalent Molecules"

Effective Completion Date: 3/31/83 (Performance) 6/30/83 (Reports)

Grant/Contract Closeout Actions Remaining:

- ☐ None
- ☒ Final Invoice or Final Fiscal Report
- ☐ Closing Documents
- ☒ Final Report of Inventions
- ☒ Govt. Property Inventory & Related Certificate
- ☐ Classified Material Certificate
- ☐ Other _____

Continues Project No. _____ Continued by Project No. _____

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GEORGIA TECH RESEARCH INSTITUTE
ADMINISTRATION BUILDING
GEORGIA INSTITUTE OF TECHNOLOGY
ATLANTA, GEORGIA 30332

Telex: 542507 GTRIOCAATL
Fax: (404) 894-3120

Phone: (404) 894-4814

February 10, 1981

Dr. John S. Showell
Program Director for Synthetic
Organic and Natural Products Chemistry
National Science Foundation
Washington, D.C. 20550

Subject: NSF Grant No. CHE-7900923

Dear Dr. Showell:

In accordance with NSF requirements, we are pleased to submit herewith two copies of a continuation proposal to Grant No. CHE-7900923, along with three copies of the proposed budget.

Please contact Dr. E. M. Burgess, the Principal Investigator, if further information is desired.

We look forward to the results of your evaluation.

Very truly yours,

Phyllis R. Oliver
GEORGIA TECH RESEARCH INSTITUTE

car
Addressee: As stated
Enclosures: Proposal - in duplicate
Budget - in triplicate

bxc: E. M. Burgess
J. A. Bertrand
H. S. VALk
File
Diary
PID
Photolab (2 copies) ✓

Interim Technical Report
NSF Grant CHE-7900923
New Functional Groups and Hypervalent Molecules

1. We estimate that no funds will remain unexpended or uncommitted at the end of the current support period (Sept. 30, 1981).
2. Current Support and Pending Proposals.

Agency - N.I.H.

Project Title - The Chemistry of New Functional Groups in Enzymes

Annual Award - \$59,783 for period 03/01/81 - 02/28/82

Support Recommended for Balance of Project

Period \$62,605 for period 03/01/82 - 02/28/83

% Effort Acad. 12.5%

Summer 100%

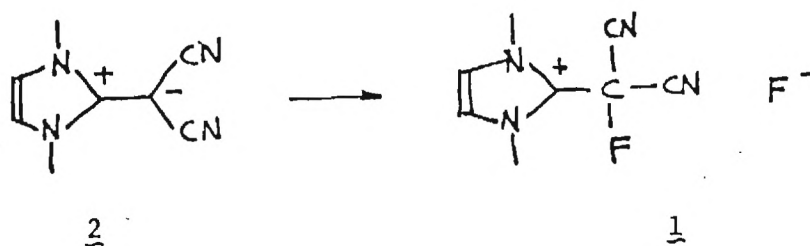
We have no pending proposals other than this request.

3. Progress Report:

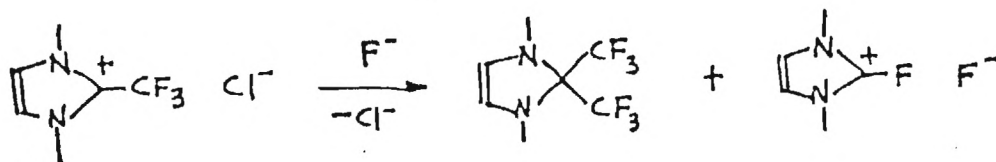
The numbering of topics in this report follows from our proposal.

1. Hypervalent First and Second Row Molecules.

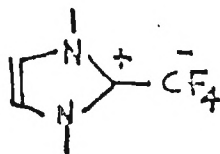
The structure of the product, 1, resulting from the reaction of the 1,2-dipole, 2, with CF_3OF has been determined by NMR F^{19} spectroscopy to have non-equivalent fluorines. This would seem to end our search



for hypervalent carbon. In one last attempt, we carried out the following reaction and obtained the result indicated.



No evidence for the hypervalent species, 3, was forthcoming.

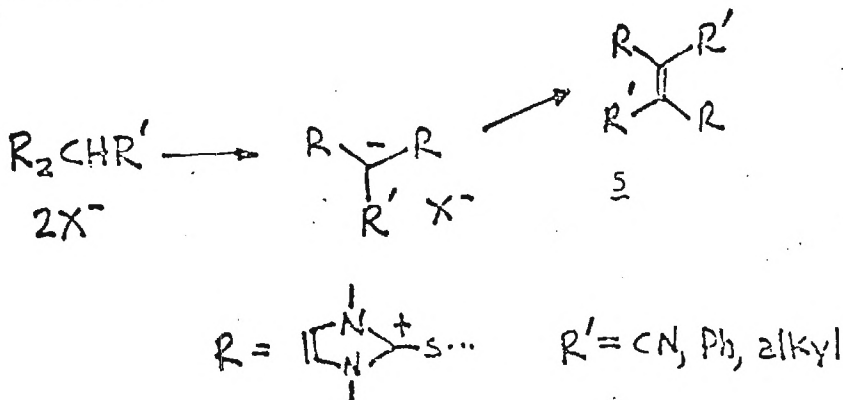


3

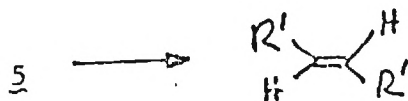
2. Thione Ylides

(a.) Ylides from Bis-thioimidazolium salts.

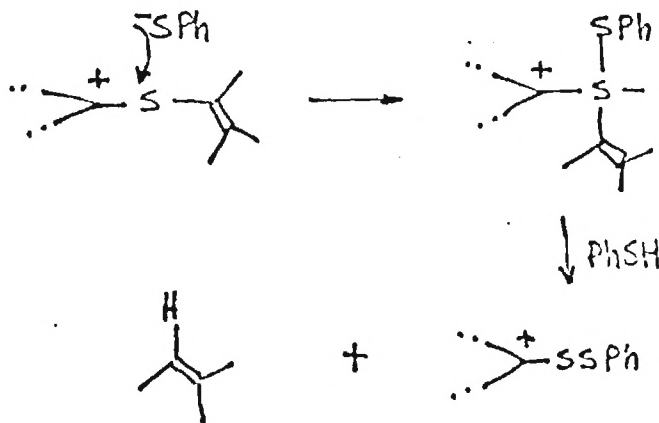
The reaction of gem-dihalides with dimethylimidazoethione give the corresponding bis-salts, 4, whose base catalyzed decomposition give the substituted ethylene derivatives, 5, at temperatures of 30-80°.



This coupling reaction would have some synthetic utility if the following transformation of the produce 5 could be developed.

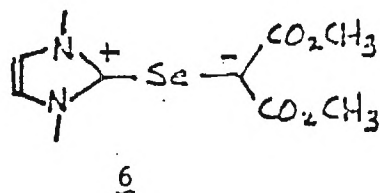


and we are currently studying the reaction of 5 with "soft" nucleophiles such as PhSH, PhS⁻ or PhSeH, PhSe⁻ with the hope of finding a reaction:

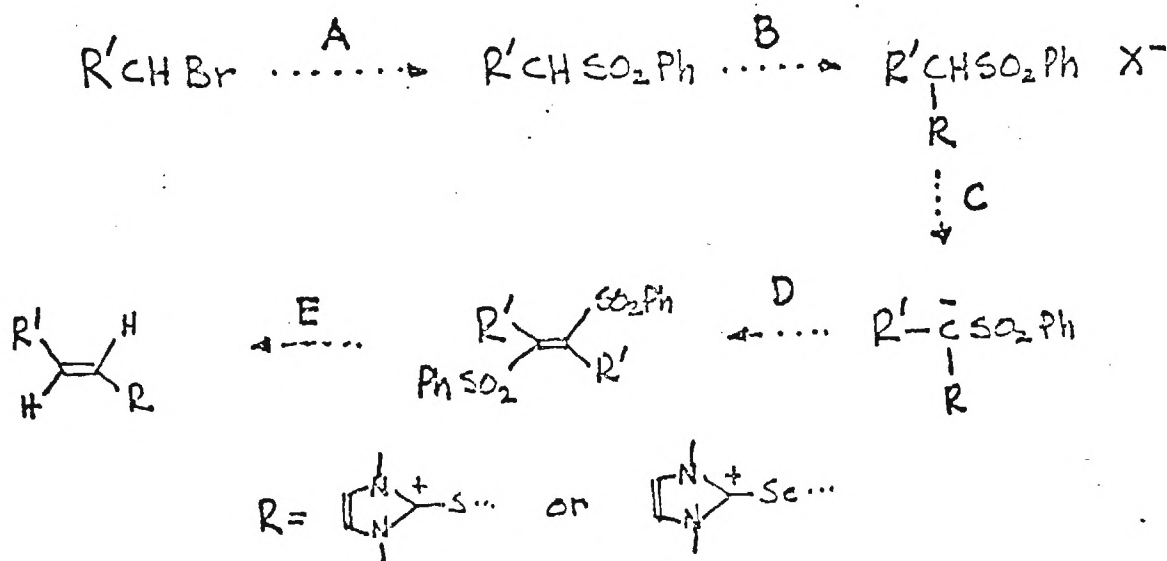


(b.) Selenone Ylides

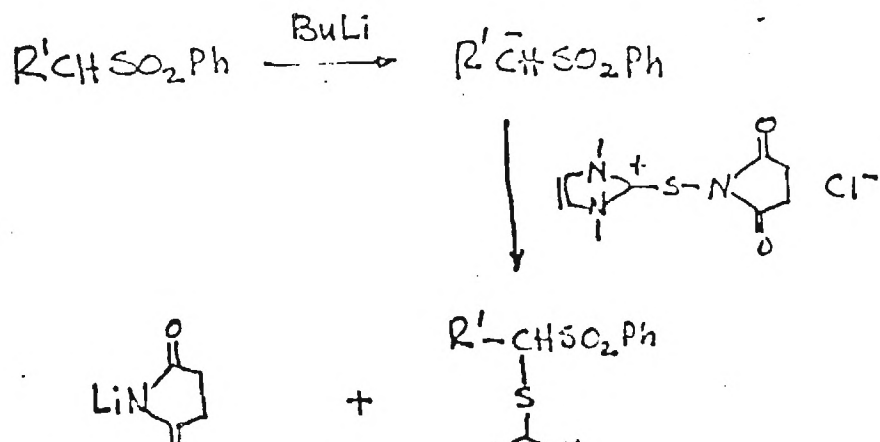
The first example, 6, of a stable selenone methylide has been isolated and characterized by x-ray crystallography. The non-planarity of substituents about the CSeC plane was similar to that



CSeC plane was similar to that previously determined for the corresponding sulfur ylides. Such selenium derived ylides decompose in solution to tetra substituted ethylene derivatives at temperatures much below (0-30°) those of the sulfur congener. As in (a.) above we are currently looking into this coupling reaction as a general C=C bond formation synthetic method. Some reactions now under investigation are:



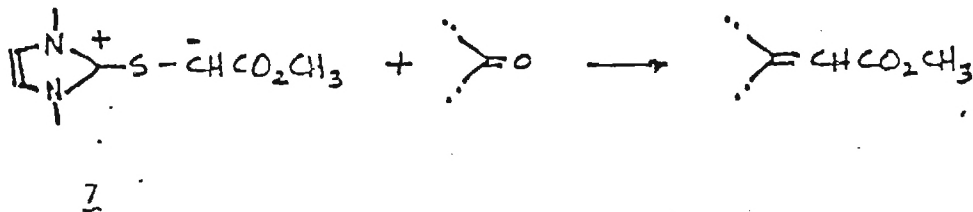
steps A and E are well known and we have carried out step B via:



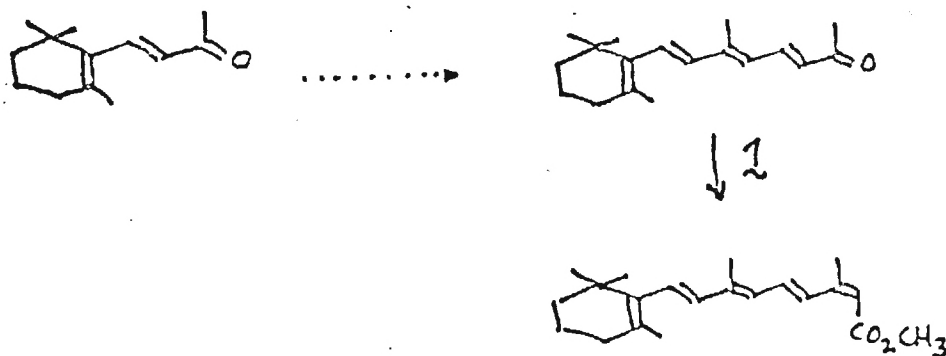
3. Synthetic Application of Hypervalent Intermeidates

(a.) Thione Methylides

We have discovered the reaction conditions (time, temperature) which effect the "pseduo" wittig reaction of 7 with ketones (formerly only a reagent for aldehydes).

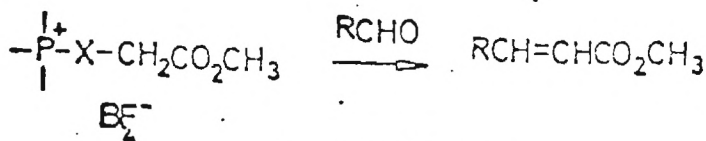
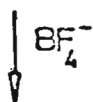
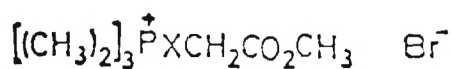
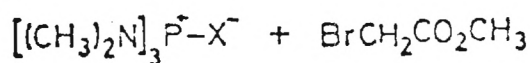


This will allow us to proceed toward the synthesis of the important agent (for severe acne and possibly useful as an antineoplastic agent) 13-cis-retenoic acid. We have begun, as follows:



(b.) Phosphile Sulfide and Selenide Methylides

We have extended our studies on the reaction of the title ylides with aldehydes and found the stereochemistry of the acrylate ester product to be a function of the method of generating the ylide (below).



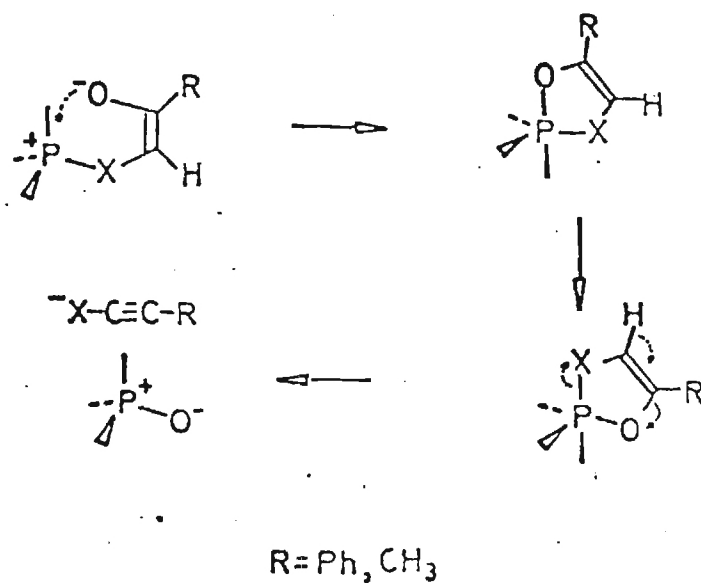
- A. DBU, CH₃CN
- B. DBU, CH₃CN, LiI
- C. NaOH, H₂O, CH₂Cl₂, Et₃N⁺ Cl⁻
- D. NaOEt, EtOH

R=Ph

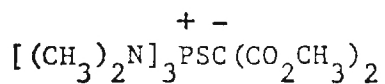
	X = S		X = Se	
	Z	E	Z	E
A	60	40	60	40
B	75	25	98	2
C	70	30	50	50
D	0	100	50	50

Thus, a stereospecific formation of either isomer may be selected using as variables the central atom of the ylides or its method of preparation. Interestingly, ylides generated with ketone stabilizing substituents (rather than ester) undergo the following internal rearrangement and fragmentation faster than reaction with

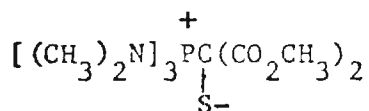
an external aldehyde. We can offer no explanation for this.



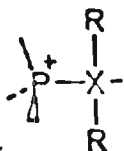
In another study, we attempted the isolation of a phosphine sulfide methyllide,



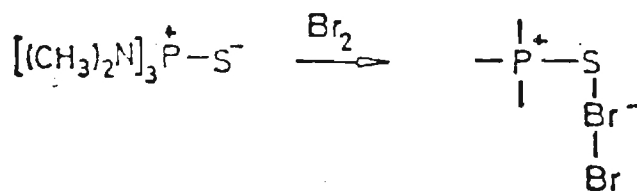
however, after a few hours in solution this ylide underwent re-arrangement to



Finally, in an attempt to generate an isolable hypervalent species:



we subjected tri-dimethylaminophosphine sulfide to bromination. The product isolated and characterized by x-ray crystallography is shown below.



(SEE INSTRUCTIONS ON
REVERSE BEFORE
COMPLETING)

3rd Year
SUMMARY
PROPOSAL BUDGET

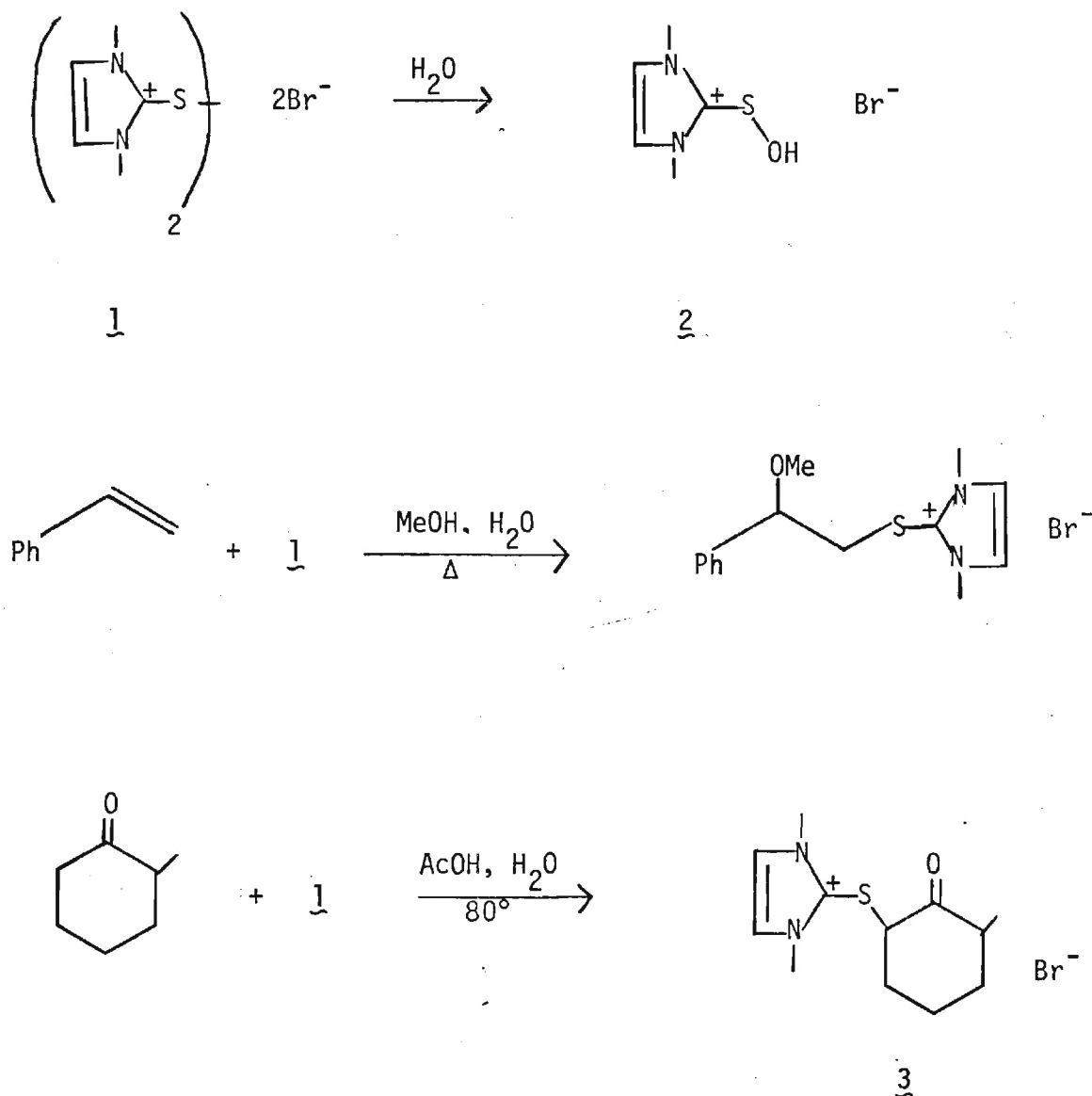
G-33-643 (cont. of)

ORGANIZATION GEORGIA TECH RESEARCH INSTITUTE				FOR NSF USE ONLY			
				PROPOSAL NO.		DURATION (MONTHS)	
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR E. M. Burgess				AWARD NO.		Proposed	Granted
A. SENIOR PERSONNEL: PI/PD, Co-PI's, Faculty and Other Senior Associates (List each separately with title; A.6. show number in brackets)				NSF FUNDED PERSON-MOS.	FUNDS REQUESTED BY PROPOSER	FUNDS GRANTED BY NSF (IF DIFFERENT)	
				CAL.	ACADSUMR		
1.						\$	\$
2.							
3.							
4.							
5. () OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)							
6. () TOTAL SENIOR PERSONNEL (1-5)							
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)							
1. () POST DOCTORAL ASSOCIATES							
2. () OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)							
3. <u>1.5</u> GRADUATE STUDENTS						12,300	
4. () UNDERGRADUATE STUDENTS							
5. () SECRETARIAL CLERICAL							
6. () OTHER							
TOTAL SALARIES AND WAGES (A+B)							
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)							
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A+B+C)							
D. PERMANENT EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING \$1,000; ITEMS OVER \$10,000 REQUIRE CERTIFICATION)							
TOTAL PERMANENT EQUIPMENT							
E. TRAVEL 1. DOMESTIC (INCL. CANADA AND U.S. POSSESSIONS)						800	
2. FOREIGN							
F. PARTICIPANT SUPPORT COSTS							
1. STIPENDS \$							
2. TRAVEL							
3. SUBSISTENCE							
4. OTHER							
TOTAL PARTICIPANT COSTS							
G. OTHER DIRECT COSTS							
1. MATERIALS AND SUPPLIES						6,013	
2. PUBLICATION COSTS/PAGE CHARGES							
3. CONSULTANT SERVICES							
4. COMPUTER (ADPE) SERVICES							
5. SUBCONTRACTS							
6. OTHER							
TOTAL OTHER DIRECT COSTS							
H. TOTAL DIRECT COSTS (A THROUGH G)						19,113	
I. INDIRECT COSTS (SPECIFY)							
46.5%							
TOTAL INDIRECT COSTS						8,887	
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)						28,000	
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECTS GPM 252 AND 253)						-0-	
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)						\$ 28,000	\$
PI/PD TYPED NAME & SIGNATURE E. M. Burgess				DATE 2/10/81	FOR NSF USE ONLY		
INST. REP. TYPED NAME & SIGNATURE Phyllis R. Oliver				DATE 2/10/81	INDIRECT COST RATE VERIFICATION		
				Date Checked	Date of Rate Sheet	Initials - DGC	

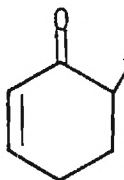
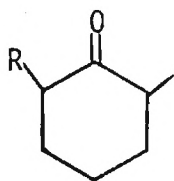
I. Technical Report

1. Thione Ylides

We have continued our investigation on derivatives of thione ylides including some new reactions of the disulfide 1. In the presence of one equivalent of water 1 is presumably transformed into the electrophilic species 2 which is capable of reaction with alkenes and enols as illustrated below. The formation of 3 derived from the less stable enol of

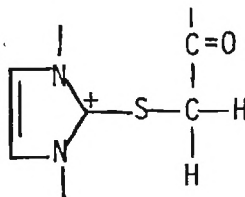


methylcyclohexanone is interesting and we are currently investigating its transformation to such inaccessible model compounds as:

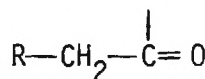


R = alkyl, aryl

which illustrate a potential synthetic use for 1. Furthermore, we found that salts with the general structure 4 react efficiently at -78° with alkyl and aryl lithium compounds to give the α -substitution product 3 in high yield.

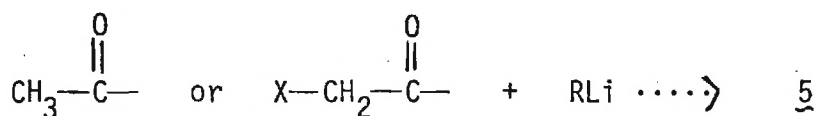


4



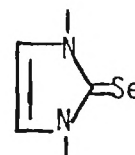
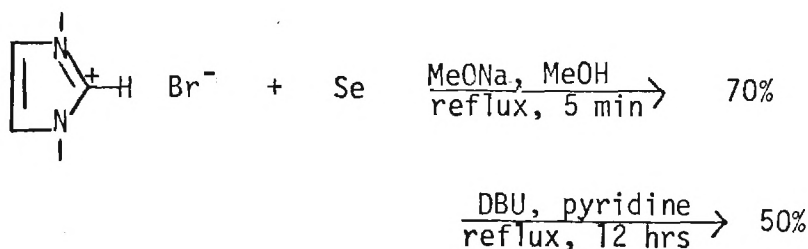
5

This reaction, which probably proceeds via a single electron transfer, homolysis, and radical pair combination provides an excellent vehicle for the transformation:



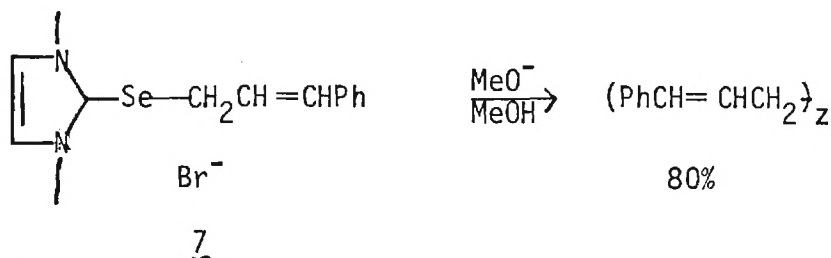
2. Selenone Ylides

We have initiated studies upon the chemistry of substituent stabilized selenone Se-methylides. The precursor selenone 6 has been prepared by the following reactions:

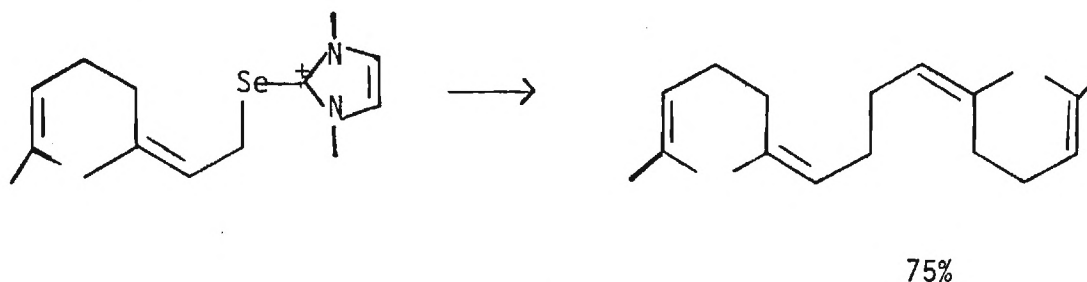


6

and readily reacts with alkyl halides to give salts. First, we investigated the base catalyzed deprotonation of such salts derived from allylic halides such as 7. Rapid formation of the reductively coupled allylic system occurred.

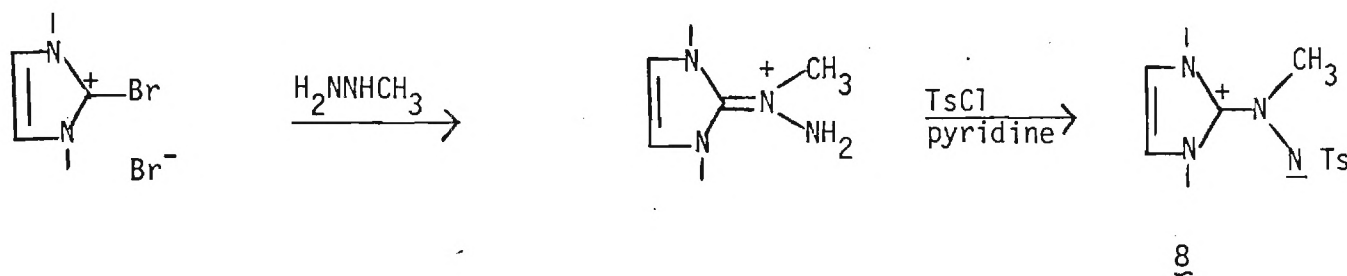


Although the mechanism of this novel reaction remains obscure its synthetic utility is obvious. We have coupled geranyl bromide by this route and are currently studying the farnesyl unit as a precursor to a squalene synthesis.

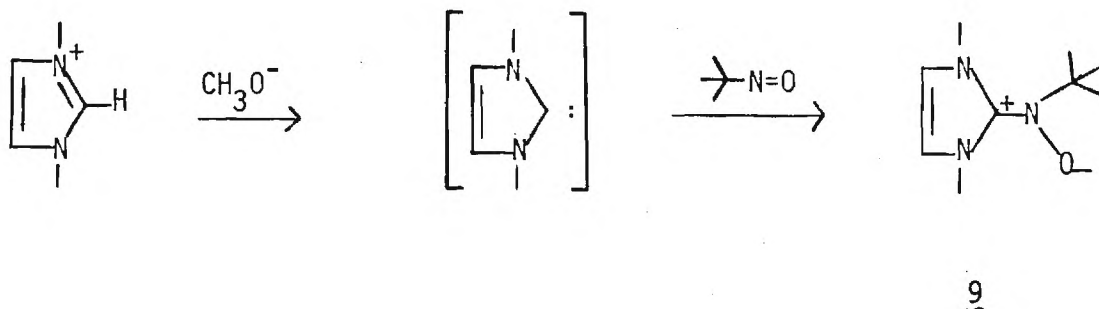


3. First Row Central Atom Ylides

We have prepared the very stable substituent stabilized azomethine imine, 8, via the following route:



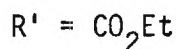
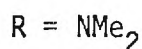
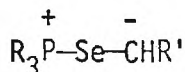
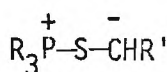
The corresponding nitron 9 resulted from the reaction:



Both 8 and 9 exhibited a ^1H -nmr singlet for the imidazole N-Me groups at room temperature and therefore are truly 1,3-dipoles. No photochemistry or thermal reactions of these ylides have been investigated to date.

4. Synthetic Application of Hypervalent Intermediates. The Wittig Reaction.

We have made considerable progress in studies of the Wittig Chemistry of the two new classes of 1,3-dipoles, Phosphine S-methylides (10) and Phosphine Se-methylides (11).



The requisite precursor salts were obtained via reaction of the phosphine sulfide or selenide with iodoacetic ester in the presence of aqueous sodium fluoroborate. Deprotonation of these salts with sodium methoxide, sodium hydroxide or DBU gave the transient ylides, 10 or 11, which react readily with aldehydes to give the corresponding substituted α,β -unsaturated ester in 70-80% yield. The stereochemistry of this reaction is as follows:

<u>ylide</u>	<u>cis</u>	<u>trans-</u>
<u>14</u>	50%	50%
<u>15</u>	60%	40%
<u>15</u> + LiI	95%	5%

We are currently investigating the analogous reaction with ketones and plan a synthesis of some vitamin A analogous such as esters of cis-retenoic acid.

II. Estimated Remaining Funds

We expect to have no remaining funds at the end of the period for which the NSF is currently providing support.

III. Current Support and Pending Proposals

We have no pending proposals other than this request.

Current support of Edward M. Burgess, Principal Investigator

Agency - N.I.H.

Project Title - The Chemistry of New Functional Groups in Enzymes

Annual Award - \$57,121 for period 03/01/80 - 02/28/81

Support Recommended for

Balance of Project

Period -

\$59,783	03/01/81 - 02/28/82
62,605	03/01/82 - 02/28/83

% Effort

ACAD.	12.5%
SUMM.	100%

Location

Georgia Institute of Technology

Grant CHE-7900923

New Functional Groups and Hypervalent Molecules

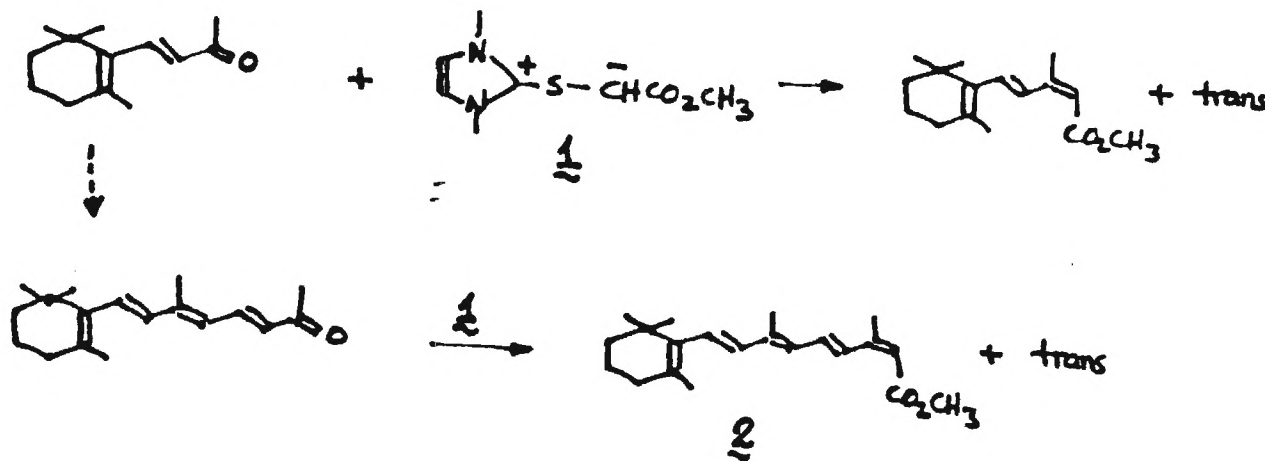
Edward M. Burgess
School of Chemistry
Georgia Institute of Technology

10/1/79 - 3/1/83

Final Progress Report

1. Wittig Reactions of Thione Methylides. The Synthesis of 13-cis Retenoic Acid

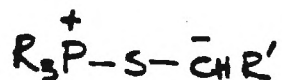
We have optimized the conditions for reaction of the ylide, 1, (generated in situ) with ketones. In model studies, using DBU as the base and acetonitrile solvent the stereochemistry of the quasi-Wittig is predominately cis (cis/trans, 3:1)



Extension of this reaction to 13-cis retenoic ester, 2, gave the stereoisomeric products in a cis/trans ratio of 2:1. LiBI_4 was added in an attempt to increase the amount of cis-product as had been previously observed in the reaction of 1 with aldehydes. Since the reaction of 1 with ketones is much slower than with aldehydes the added salt resulted in demethylation.

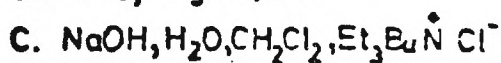
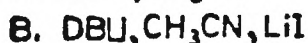
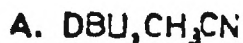
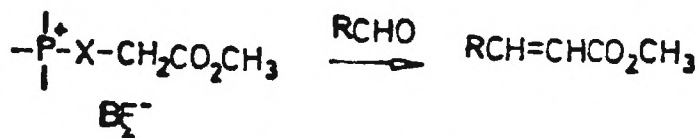
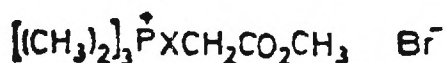
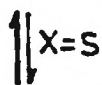
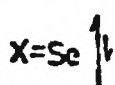
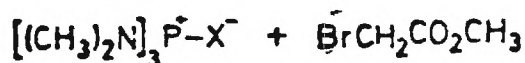
2. New Wittig Reagents

We have made considerable progress in studies of the Wittig Chemistry of the two new classes of 1,3-dipoles, Phosphine S-methylides and Phosphine Semethylides:



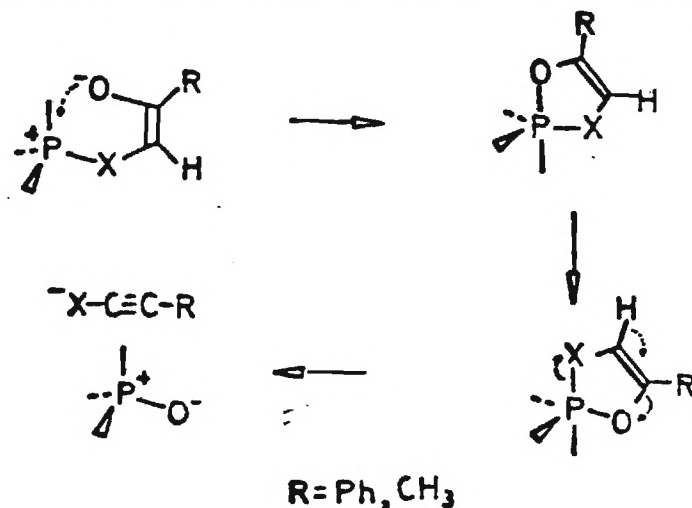
The requisite precursor salts were obtained via reaction of the phosphine sulfide or selenide with iodacetic ester in the presence of aqueous sodium fluoroborate. Deprotonation of these salts with sodium methoxide, sodium hydroxide or DBU gave the transient ylides, 14 or 15, which react readily with aldehydes to give the corresponding substituted α,β -unsaturated ester in 70-80% yield.

Studies on the reaction of the title ylides with aldehydes found the stereochemistry of the acrylate ester product to be a function of the method of generating the ylide (below).

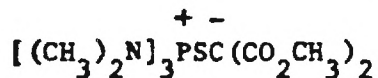


		R=Ph	
		X=S	X=Se
		Z	E
A		60	40
B		75	25
C		70	30
D		0	100

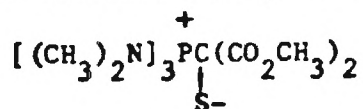
Thus, a stereospecific formation of either isomer may be selected using as variables the central atom of the ylides or its method of preparation. Interestingly, ylides generated with ketone stabilizing substituents (rather than ester) undergo the following internal rearrangement and fragmentation faster than reaction with an external aldehyde. We can offer no explanation for this.



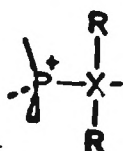
In another study, we attempted the isolation of a phosphine sulfide methyllide,



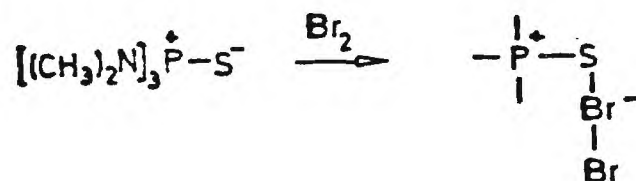
however, after a few hours in solution this ylide underwent rearrangement to



Finally, in an attempt to generate an isolable hypervalent species:



we subjected tri-dimethylaminophosphine sulfide to bromination. The product isolated and characterized by x-ray crystallography is shown below.



3. Oxidative Chemistry of Disulfides

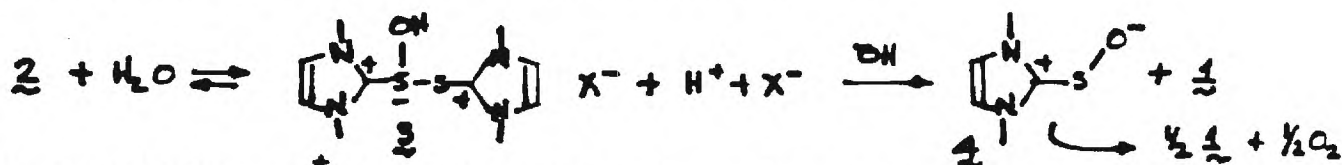
The reaction of 1,3-dimethylimidazolthione (1) with 0.5 equivalent of bromine at 0°C in methylene chloride solution gives the disulfide, $2(X=Br)$, mp 240-241°C (dec.) as published in J. Amer. Chem. Soc., 99, 2376 (1977).



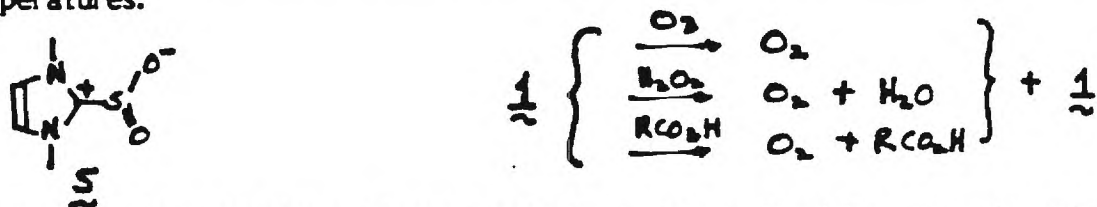
The following observations in the chemistry of 2 have not been published.

By suitable anionic exchange procedures, various salts ($X=Cl^-$, BF_4^- , $OSO_2CF_3^-$) are available and the triflate salts have good solubility in acetonitrile and are suitable for aprotic solvent reactions. All salts are water soluble. When any one of these salts is dissolved in water the pH drops to 2. Evaporation of the water gives back quantitatively 2. Addition of base (sodium hydroxide, sodium carbonate, sodium bicarbonate) to the aqueous solutions of 2 gives dioxygen and 1. No intermediate could be detected by NMR analysis in D_2O . By polarography the onset of a detectable oxygen wave occurred at pH = 4.5 and the reaction is very fast at pH 6.0. Using a single cell consisting of two Pt-electrodes and an aqueous solution of a neutral electrolyte (such as NaCl) the potential across the electrodes was adjusted just below the threshold for visible gas formation at either electrode. Addition of 2 to this cell at this potential led to immediate formation of gasses at both electrodes. No quantitative measurement has been made of the efficiency (O_2 production vs. time vs. potential) in this cell with and without 2, but the above qualitative observation suggests that 1 may function as a catalysis for the electrolysis of water at advantageous cell voltages. It has been demonstrated that 1 is oxidized to 2 at a working anode in aqueous solution containing HCl at pH 1-2.

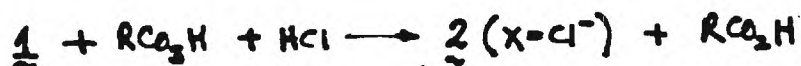
The exact mechanism of this reaction is unknown but the following observation suggest a few key intermediates. As a model the first step in the reductive hydrolysis of 2 may be 2 in agreement with pH observation in water. The ability of a imidazolium substituent to stabilize hypervalent bonding at sulfur is discussed in the enclosed preprint. Action of base on 3 may give 4 which disproportionates to oxygen and 1.



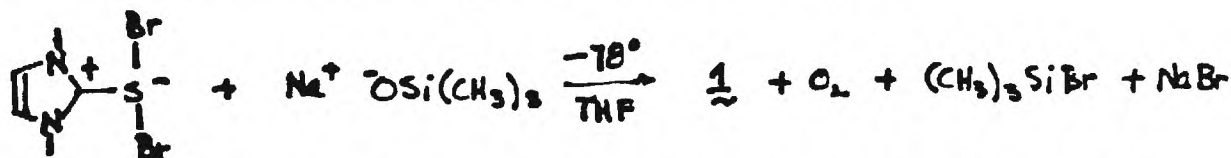
Simple sulfoxides, $\text{R}_2\text{S-O}^-$, are known to undergo disproportionation to sulfides, R_2S , and sulfones, R_2SO_2 at elevated temperatures and in the case of 4 this may be a facile reaction leading to 5. If this is the case then 5 must also rapidly give oxygen and 1. In order to gain some support for this mechanistic model the action of various oxidizing agents on 1 to hopefully give 4 or 5 was investigated. In all cases examined (below) the oxidizing agent was catalytically converted to oxygen at fast rates even at low temperatures.



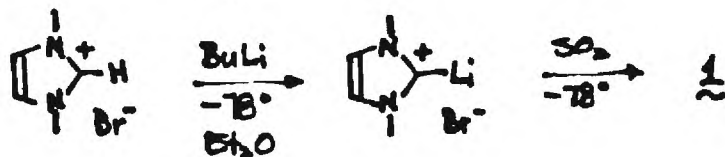
However, if the oxidation of 1 was carried out at low pH with a percarboxylic acid the result was 2.



Even more esoteric methods of obtaining 4 led to a similar observation.



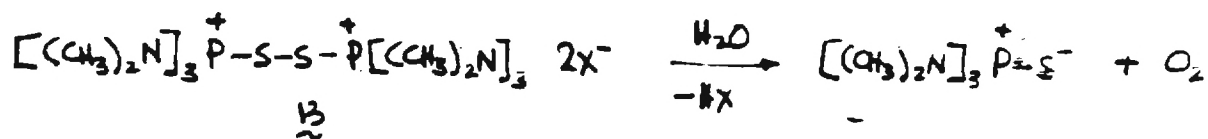
In other attempts to obtain 5 the reaction of lithio-derivative 6 with sulfur dioxide led to the formation of 1.



Details of this observation are discussed in the enclosed preprint.

We may conclude that 5 rapidly gives 1 and oxygen and that 4 may also give 1 and oxygen possibly via its transformation to 5. All of these reactions appear to proceed at rapid rates even at low temperatures and thus represent a reaction sequence with no large energy of activation single steps.

This class of reaction is not limited to 6. Oxidation of tris(dimethylamino) phosphine sulfide, 13, with NOBF_4 gives a disulfide which also oxidizes water.



Publications:

1. None in Print
2. The enclosed preprints are submitted to the J. Amer. Chem. Soc. (The Conversion of Thiourea Dioxides to Dioxygen) and the J. Org. Chem. (Substituent stabilized Thione S-Inides).
3. We contemplate a publication on the phosphine S- and Se- methylides as well as one on the retenoic acid study.

The Conversion of Thiourea Dioxides to Dioxogen

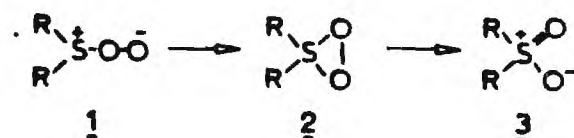
Edward M. Burgess*, U. Zoller and R.L. Burgen, Jr.

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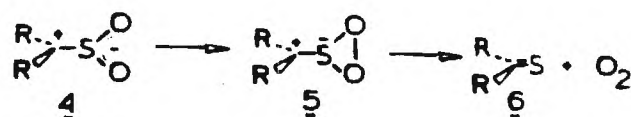
Received

Abstract: Dimethylimidazole thione 1,3-dioxides was prepared from dithione amide and 2-lithio dimethylimidazolium salts and found to decompose to oxygen and the corresponding thione. *N,N*-Dimethylthiourea 1,3-dioxides and related thiourea and amide upon heating in acetonitrile solution. Dimethylaminophosphine reacts with sulfur dioxide to produce phosphine oxide and sulfide. These reactions are discussed in terms of an intermediate singlet sulfurane which fragments to triplet oxygen, via a reverse crossing process.

From both a biological¹ and chemical viewpoint the oxygen and sulfur section of 1,2- and 1,3-dipoles² containing one or more oxygen atoms have received considerable recent attention. Prominent among these reactive intermediates are persulfuranes, 1, which result from the action of hydrogen peroxide on sulfides³ or hydrogen peroxide on fluoro derivatives of allylsulfuranes.⁴ It has been shown that 1 (R = allyl) has the ability to transfer an oxygen atom to sulfides to give sulfoxides and more rapidly to sulfones. If 1 is derived from the dihalosulfurane, its electrophilicity is sufficient to effect epoxidation of alkenes.⁵ In the absence of oxidizable reagents, 1 is ultimately converted into the thione, 3, possibly via the electrocyclic product, the hypervalent dioxirane 2. From studies of the solvent effects on the efficiency of oxygen atom transfer the primary species present seems to be 1.^{6,7} However, when 1 (R = Ph) is generated via the sulfurane route in the presence of a triplet energy acceptor such as 9,10-dibromopanthracene, chemiluminescence of the latter is observed.⁶ This suggests that 3 is derived from 2 in a triplet state. Clearly, the reaction sequence connecting 1 and 3 is most unique and deserves further study.



Employing rather Edisonian reasoning we were convinced of the possibility that the reaction above could be reversed exothermically, i.e., $3 \rightarrow 2 \rightarrow \text{O}_2$. If 3, by proper substitution, would have less thermodynamic stability than 2, such a reversal might be realized. With the knowledge⁷ that an electron acceptor substituent with an energetically low-lying unoccupied molecular orbital (LUMO) of the π -type attached to sulfur stabilizes a tricoordinate hypervalent sulfurane bonding arrangement, a possible forward reaction might be the sequence $4 \rightarrow 5 \rightarrow 6$. In this communication we wish to describe our observations on this strategy using an imidazolium or a dimethylamino group to properly adjust the carbonium ion substituent LUMO energy.



- a, R = $\begin{array}{c} | \\ \text{N} \\ | \\ \text{N} \\ | \end{array}$
- b, $\text{Me}_2\text{N}-$
- c, NH_2-
- d, $n\text{-BuNH}-$

It has been reported that bisaminocyclopropanium⁴ and pyrazolium⁵ salts may be lithiated by *n*-butyllithium or chloromethyl lithium⁶ at low temperatures to give substituted substituted thiocarbocation ions which readily undergo SE reactions with electrophiles. Following these observations, in order to prepare **4a** we heated an anhydrous diethyl ether suspension of N,N-dimethylthiocarbonyl amide under an argon atmosphere with an excess of *n*-butyllithium (1.1 M in hexane) to give **7a**. After 6 hours at 30° sulfur dioxide was introduced and upon standing for 20 hours unreacted starting material, lithium bromide, **7a** was isolated (quantitative yield based on a 36.6% conversion).¹⁰ trace of the urea. **8a** could be detected and if **4a** was an intermediate was converted only to **6a** (no effort was made to establish that **6a** was a product).

Monocyclic and trialkylthiourea S,S-dioxides have recently been prepared¹¹ and the unsubstituted thiourea S,S-dioxide, **4c**, is a well known industrial reducing agent in aqueous solution. Curiously, no reports have appeared of the thermal decomposition of these dioxides in aprotic solvents. Only that solid N,N'-di(*sec*-butyl)thiourea S,S-dioxide decomposes to sulfur dioxide and the corresponding formamidine at 100° or that **4c** gives analogous products in refluxing acetic acid.¹⁴

We find that **4c** decomposes to thiourea, urea (2:3 ratio) and dithioamide in refluxing anhydrous acetonitrile with a 98% conversion after 0.7 hours, from nmr kinetic analysis. **6d** (mp. 85-6° (dec.))¹² was prepared by the hydrogen peroxide oxidation of N,N'-di(*n*-butyl)thiourea according to standard published procedures.¹¹ This derivative in acetonitrile provided the thiourea and formamidine (1:2.8 ratio) in a first order reaction with composite $k_1 = 1.0 \times 10^{-4}$ ($r = 0.9972$) at 45°.

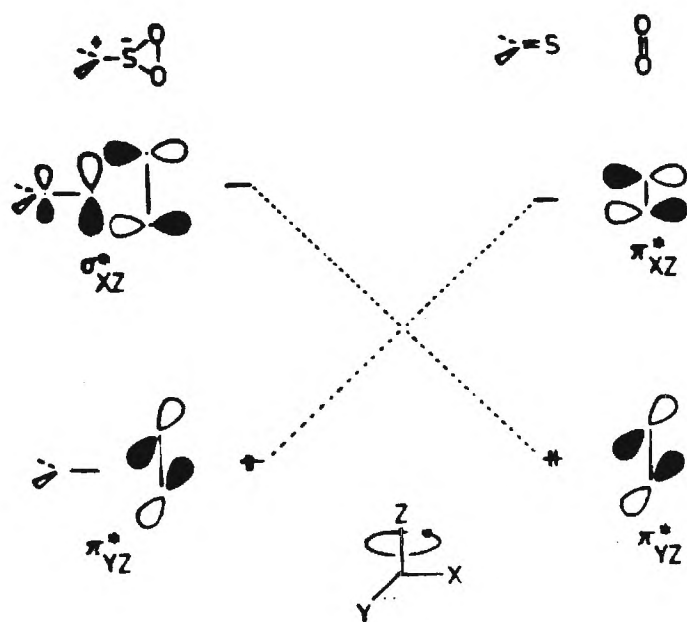


Figure 1. Orbital Correspondence for the Fragmentation of a Hypervalent Substituted Thiadioxirane to Dioxide. Rotation of the O-O fragment occurs about the z-axis.

SCF-MO calculations reveal that the lowest energy mode of decomposition is dissociation into the singlet carbene and sulfur dioxide complex (bond length of 2.05 Å) lying only 2-3 kcal. above the bound dioxide. This result accounts for the equilibrium of **7a** and sulfur dioxide with **4a** leading to isolation of a considerable amount of starting imidazolium salt after 20 hours. The formidine isolated in the decomposition of **4d** also may be ascribed to tautomerization and loss of sulfur dioxide from this complex. Interestingly, this reaction is also theoretically characterized as a molecular orbital level¹² at a higher activation energy by the linear departure (mirror symmetry about an xy-plane) of a singlet dioxygen fragment from singlet **5**. Along this fragmentation reaction coordinate, a coupled-occupied-unoccupied orbital crossing occurs if a rotation about the z-axis of oxygen p_y- and p_x-orbitals is assumed. This provides the orbital product correspondence (the stationary thione fragment acting as an orbital symmetry reference) shown in Figure 1¹⁴. At this crossing point the orbital rotation creates orbital angular momentum along the z-axis which is favorable for a large spin-orbit coupling matrix element between the triplet and singlet state. Intersystem crossing to the triplet reacting complex occurs to give exothermically the lower energy triplet dioxygen. This is an unique example, unlike most forbidden pericyclic reactions, in which the triplet surface remains energetically below the singlet beyond the crossing point (Figure 2).

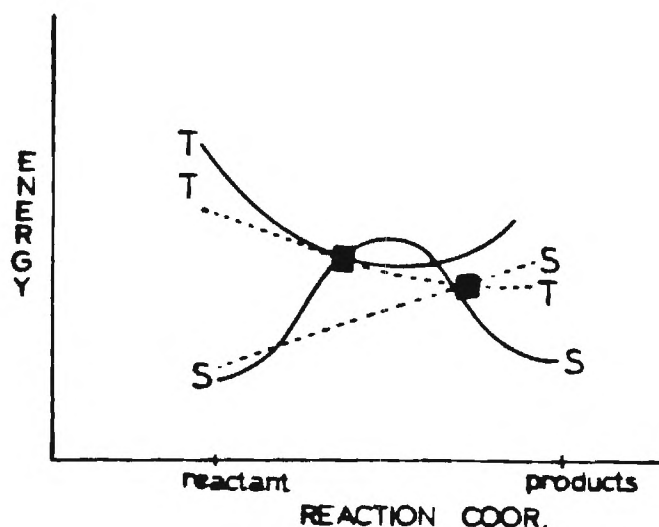
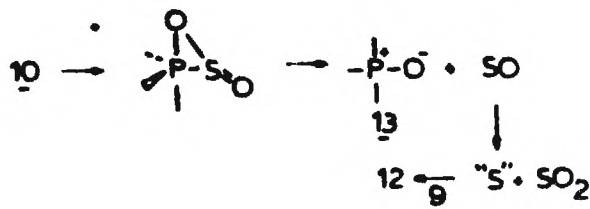
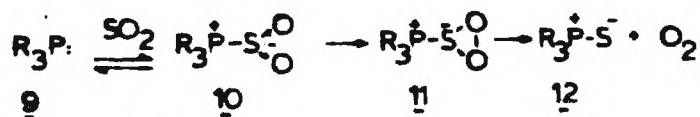


Figure 2. The Surfaces for Pericyclic Reactions. S is the lowest singlet state (ground state) and T the lowest triplet state. The solid line represents the path with two crossing points associated with most forbidden pericyclic reactions. The dotted line is characteristic of reactions producing a stable ground state triplet product such as dioxygen. If both states have the same symmetry intersystem crossing may occur in the shaded regions.

If intersystem crossing occurs before the rate determining step transition state the production of the triplet product might be enhanced e.g. an external heavy atom effect. Unfortunately, we could find no change in product yield or decomposition of **6d** in the presence of mono- or di-iodobenzene. This suggests that the crossing point does not meet the above criterion or that the internal orbital motion produces a torque leading to a coupling geometrical alignment which is much greater than any external heavy atom can provide.

Finally, another substituent with an energetically low-lying unoccupied orbital of the π^* -type which would stabilize a tricoordinate sulfur radical binding system is the phosphonium group. We explored the possibility of the reaction **9** \rightarrow **10** \rightarrow **11** \rightarrow **12**.



the treatment of **9**¹⁷ (neat) with an excess of sulfur dioxide at -78° gave a 72% yield of the phosphine oxide (**13**) and sulfide (**12**) in a ratio 3:4.¹⁸ A 1:1 mixture of **12** and **13** could be accounted for by the reaction below¹⁹ without the intervention of **11** and its subsequent fragmentation. However, when this reaction was carried out under the same conditions in the presence of an equimolar amount of *o*-dibromodiphenyl sulfide was unchanged but the ratio of **13** to **12** was 3:7. It is amusing to speculate that in this case an external heavy atom catalyst was responsible for an increased intersystem crossing efficiency in the fragmentation of intermediate such as **11**.

Acknowledgement

We wish to thank the NSF and NIH for generous financial support and Dr. Charles Liotta and Kent Barefield for their interest and suggestions.

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- C.D. Lloyd and H. McNab, *ibid.*, **15**, 459 (1976).

At no time did the reaction mixture become homogeneous. Neither *N*-dimethylimidazolium perchlorate in methylene chloride solution or the triflate salt in THF solution give any detectable amounts of **6a** in this reaction. Traces of **6a** were found in the reaction of the triflate as a suspension in diethyl ether. The origin of this solvent effect is unknown.

W. Walter and G. Randau, *Justus Liebigs Ann. Chem.*, **722**, 80 (1967).

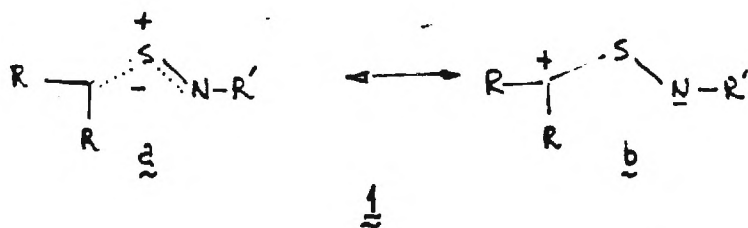
1. Identified by mass spectroscopy.
2. A satisfactory elemental analysis was obtained.
3. J.J. Havel and R.D. Klutiz, *Syn. Comm.*, 389 (1974).
4. MINDO/3 with geometry-energy optimization.
5. An excellent discussion of favorable orbital orientation for π - π bonding may be found in L. Salem and L. Rowland, *Angew. Chem. Int. Ed.*, 10, 92 (1971).
6. Kindly provided by Dr. Kent Benfield.
7. The balance of the reaction mixture was single unidentified oil containing product.
8. A similar mechanism accounts for the formation of **4c** in the isomerization of **4a**.

Substituent Stabilized Thione S-Imides. The Effect

of π -Donor Substituents on Reactivity

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Since the first successful synthesis of isolable thione S-imides, 1, (best represented by canonical structures a and b) stabilized by a combination of π -acceptor substituents¹ or a combination of π -acceptor (R') and donor (R) groups² interest in this new sulfur functional group has continued. Studies upon the three dimensional structural features³, possible geometrical isomerism⁴, photochemistry⁴, electrophilic reactions⁵, cycloadditions¹ and synthetic utility⁶ have been reported.



We undertook the synthesis of 2 and 3 in order to study some fundamental reactions of thione S-imides stabilized by various π -donor substituents but with a common π -acceptor group. Both ylides (2, m.p. 133-4° dec; 3, m.p. 185-190° dec.) were conveniently (91-94% yield)

prepared by the reaction of Chloramine-T trihydrate with the appropriate thiourea in methanol solution at 0-27°. Analogous reactions of dimethylthioformamide and 9-xanthione at -30° to -50° gave only sulfur and the corresponding N-tosylimine.

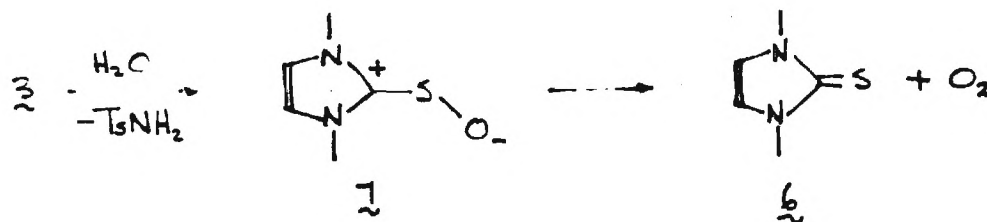
If the stabilizing substituents are inefficient in charge delocalization in either 1a or 1b the ylide structure no longer lies below the valence isomeric thiaziridine, 4, in potential energy and undergoes facile [1,3]-electrocyclization to give 4 which subsequently undergoes rapid loss of sulfur and formation of an imine, 5.^{2,4}



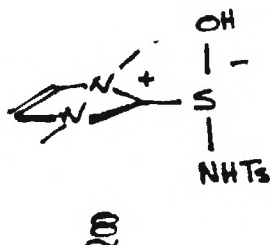
The difference in the thermal chemistry of 2 and 3 reflects this. Thione S-imide, 2, having a π -donor substituent which delocalized positive charge over a fewer number of atoms, readily (in refluxing THF or at 120° in the solid state) gives N-tosyl-N',N''-dimethylguanidine and sulfur while 3 with greater charge delocalization is stable up to 145° (refluxing o-xylene). Both 2 and 3 have unrestricted rotation about the C-S and C-N bonds in solution at room temperature as indicated by the nmr chemical equivalence of the N-methyl groups. Thus, the electrocyclization barrier is free of rotational constraints and determined primarily by the charge interaction between the termini of the 1,3-dipole.

A striking reversal of this reactivity difference is demonstrated in the hydrolysis of 2 and 3. The dimethylimidazolium substituted ylide reacts very rapidly ($t_{1/2} < 5$ min) with H₂O/MeOH at 25° to quantitatively afford N,N'-dimethylimidizolthione (6) and tosylamide while 2 is unaffected by 20% HCl in MeOH/H₂O

at 25°. It should be noted that in the observed reaction the sulfur moiety has been reduced to the thione level and the expected hydrolysis product, a thione S-oxide (7), was not present. Attempts to prepare 5 by other routes proved fruitless but interesting. Thioamides have been oxidized to the corresponding stable S-oxides by a variety of peroxo-compounds⁷. Treatment of 6 with a 10-fold excess of MCPBA in CH₂Cl₂ at 25° resulted in a vigorous evolution of O₂ and rapid formation of m-chlorobenzoic acid while 6 was recovered unchanged. Similar results occurred with aqueous H₂O₂. We must conclude that 7 undergoes a facile decomposition to dioxygen and 6 and thus the overall hydrolysis reaction of 3 may be represented by the sequence:



The difference in reactivity between 3 and 4 and the mechanism for the conversion of 3 to 4 may be explained in terms of an intermediate, 8, whose tri-coordinate central hypervalent sulfur atom enjoys considerable stabilization



by the equatorial Π -donor substituted carbocation.^{8a} If the rate of hydrolysis depends upon the transition state (product-like) leading to the hypervalent intermediate, then the stability of this intermediate and the reaction rate is a function of energetic placement of the equatorial Π -substituent. The lowest 3-center bonding orbital (σ) of the coaxial hypervalent orbital array has the proper symmetry to interact with the empty substituent orbital (p) and the magnitude of this interaction is inversely dependent upon the energy difference, $E_\sigma - E_p$ (Fig. I). The more delocalized imidazolium cation lying lower in energy is therefore more effective in stabilizing (lower energy) the hypervalent σ -bond, thus **3** is more reactive than **2**.

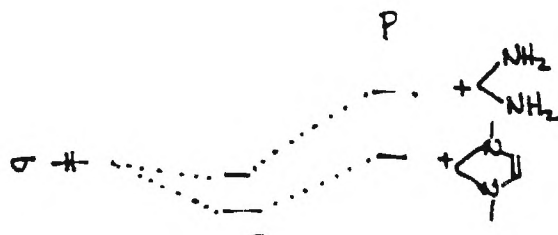
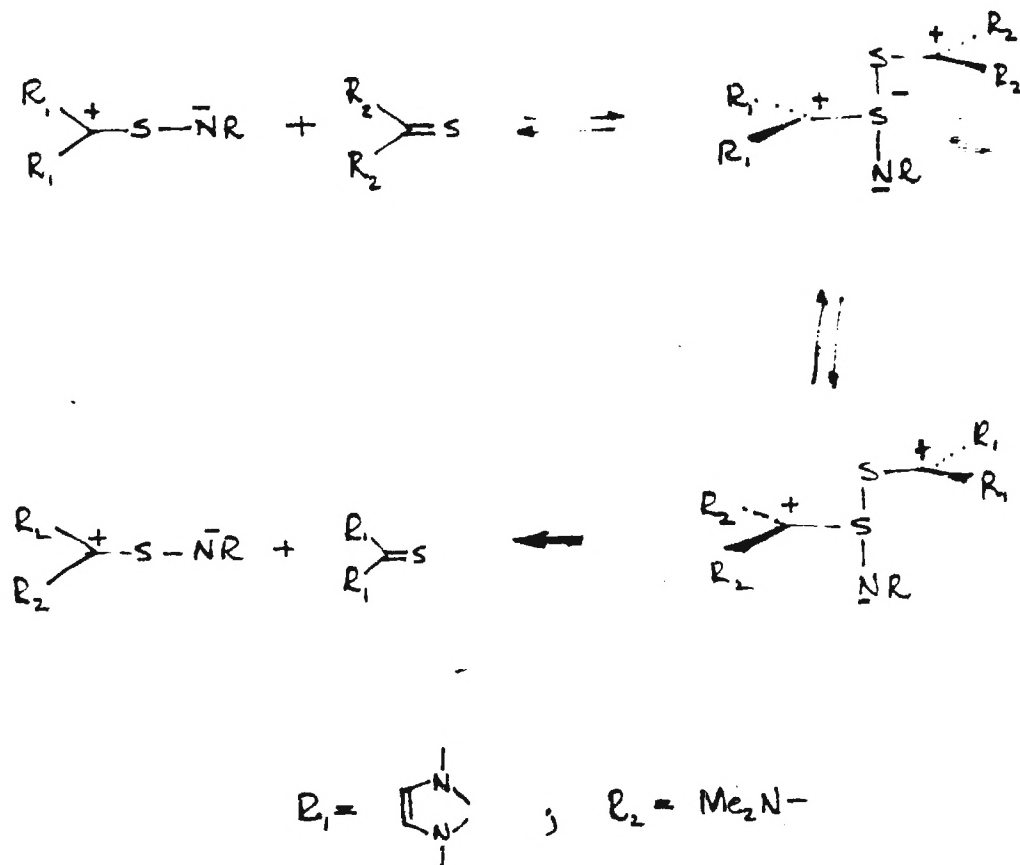


Figure I. Diagram for a hypervalent σ -bond and equatorial substituent p-orbital interaction.

The effect of the Π -donor substituent on the chemistry of ylides **3** and **2** may be demonstrated in another unusual reaction. As observed in the case of thione methylides,^{8b} treatment of **3** with tetramethylthiourea in MeCl_2 solution at 30° rapidly and irreversibly affords **4** and **5**. This substituent transfer

reaction proceeds in a direction to give the ylide with the less effective Π -donor substituent. Again, if hypervalent intermediates are involved; those with imidazolium substitution at the hypervalent sulfur atom are more stable than those with the amidinium substituent. The latter, if formed, should irreversibly undergo loss of an axial ligand. A mechanism for this exchange reaction may be:



In conclusion, substituent stabilized thione S-imides demonstrate reactions which critically depend upon the ability of the Π -donor substituent to stabilize hypervalent bonding at the attached sulfur center.

Experimental Section

Osmotic molecular weights were determined on a Mechrolab vapor pressure osmometer (model 301A) at 37°C and mass spectra were obtained on a Hitachi Perkin-Elmer RMU-7L high resolution mass spectrometer with an 80 electron volt source. Proton nuclear magnetic resonance spectra were recorded on a Varian Associates model T-60A spectrometer and chemical shifts were reported versus an internal tetramethylsilane (TMS) standard and the abbreviations s, d, t, q, and m refer to singlet, doublet, triplet, quartet, and multiplet, respectively. Carbon-13 nuclear magnetic resonance spectra were obtained on a JEOL model PFT-100 Fourier transform nmr spectrometer and the chemical shifts are reported versus a tetramethylsilane standard in the same manner as proton nmr. Infrared spectra were obtained on a Perkin-Elmer model 457 recording spectrophotometer using either 0.1 mm sodium chloride cells or a potassium bromide wafer. Ultraviolet spectra were recorded on a Beckman DB-GT spectrophotometer using one centimeter balanced quartz cells. Elemental analyses were performed by Atlantic Microlab, Inc., Atlanta, Georgia. Solids were identified by mixture melting point with authentic samples.

~~1,3-Dimethylimidazole-2-thione S-p-Toluenesulfonimide (3).~~ 1,3-Dimethylimidazole-2-thione⁹ (12.8 g, 0.1 mole) was added in a single portion to a solution of 28.2 g (0.1 mole) of Chloramine-T trihydrate in 200 ml anhydrous methanol at 27°.

The mixture was stirred for two hours and then diluted with 75 ml anhydrous methylene chloride. The reaction mixture was then filtered through celite to remove the precipitated sodium chloride. The filtrate was cooled to -78° and the crystalline product which separated was collected by filtration. The crude material was recrystallized from anhydrous methanol to give 28.0 g (94%) of the thione S-imide as colorless plates: mp 185-190° (dec.); ir (KBr) 3090 (C-H), 1260 and 900 cm⁻¹; Proton nmr (DMSO-d₆) δ 7.53 (s, 2H), δ 7.28 (q, 4H), δ 3.75 (s, 6H),

δ 2.25 (s, 3H); Carbon-13 nmr (DMSO- d_6) δ 147.1 (s), δ 122.92 (s), δ 9 (s), and δ 20.75 (s); osmotic molecular weight (CHCl_3) 299.0.

Anal. Cal. for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2\text{S}_2$: C, 48.48; H, 5.00; N, 14.14; S, 21.55. Found: 48.25; H, 5.14; N, 14.09; S, 21.38.

This S-imide was recovered unchanged after 15 minutes reflux in o-xylene.

3,3'-Tetramethyl-thiourea S-p-Toulenesulfonimide (2). 1,1,3,3-Tetramethyl-

thiourea (10.0 g 0.075 mole) in 50 ml of absolute methanol was added dropwise

over a period of one hour to 21.3 g (0.075 mole) of chloramine-T trihydrate;

dissolved in 100 ml of methanol maintained at 0°. When the addition was complete,

the reaction mixture was stirred at 0° for an additional hour, and then the pre-

cipitated sodium chloride (2.98 g) was removed by filtration. The filtrate was

concentrated with a rotary evaporator under reduced pressure to a viscous oil.

The oil was dissolved in 150 ml of methylene chloride and the remaining sodium

chloride (total yield: 4.29 g (98%)) was removed by filtration. The methylene

chloride was removed from the filtrate with a rotary evaporator under reduced

pressure to afford a clear colorless oil. While the resulting oil was rapidly

evaporated, 100 ml of anhydrous THF was added which caused 20.6 g (91%) of 1,1,3,3-

diethyl-thiourea S-p-toulenesulfonimide to separate as a colorless powder:

mp 134° (dec); uv max (CHCl_3) 243 nm (shoulder, ϵ 24,900), 272 nm (shoulder) and 300 nm (shoulder, ϵ 9840) ir (CHCl_3) 1580 ($\text{N}=\text{S}=\text{C}$), 1395 and 1165 cm^{-1}

Proton nmr (CDCl_3) δ 7.74 (d, 2H, J = 8 Hz, aromatic CH), 7.21 (d, 2H, aromatic CH), 3.12 (s, 12H, $[(\text{CH}_3)_2\text{N}]_2$) and 2.37 (s, 3H, p- CH_3); mass

m/e (rel intensity): 269 (0.6), 155 (100), 146 (6.8), 132 (10); cryo-

molecular weight (tert-butyl alcohol) Calculated: 301. Found: 288.

Anal. Calc. for $C_{12}H_{19}N_3O_2S_2$: C, 47.81; H, 6.35; N, 13.94; S, 21.28. Found: C, 47.57; H, 6.54; N, 13.76; S, 21.04.

Although λ decomposes within a few days at room temperature, it can be stored for extended periods of time if maintained at temperatures below zero degrees.

Dimethylthioformamide S-p-Toluenesulfonimide. Dimethylthioformamide¹⁰ (5.0 g, 0.056 mole) was added dropwise over a period of 30 minutes to 15.8 g (0.056 mole) of chloramine-T trihydrate in 40 ml of absolute methanol maintained at -30° . As each drop was added, a precipitate of sodium chloride formed, followed immediately by an amorphous yellow precipitate of elemental sulfur. Similar results were encountered when the temperature was lowered to -50° . When the addition was complete, the reaction mixture was cooled to -78° and 75 ml of anhydrous ether was added to cause precipitation of all products. The reaction mixture was filtered and the collected precipitate was titrated with 75 ml of anhydrous THF. The insoluble inorganic substances were removed by filtration and the filtrate was concentrated with a rotary evaporator under reduced pressure to give a colorless powder. Infrared analysis of the powder revealed the presence of p-toluenesulfonamide and a second component having a strong absorption at 1630 cm^{-1} . Fractional recrystallization with anhydrous THF separated the two compounds which were identified as p-toluenesulfonamide and N-dimethylaminomethylene-p-toluenesulfonimide (6.27 g): mp $134-135^\circ$ (lit.¹¹ mp $133-135^\circ$).

9-Xanthione S-p-Toluenesulfonimide. 9-Xanthione¹² (1.59 g, 0.0075 mole) in 35 ml of methylene chloride was added dropwise to 2.11 g (0.0075 mole) of chloramine-T trihydrate. The addition was done at various temperatures. At -30° a red intermediate formed immediately; however, it dissipated over a period of 30 seconds. At -50° the red intermediate formed at a slower rate, but it also dissipated within 30 seconds. At -78° there was no reaction. When the addition was complete,

the precipitated sodium chloride was removed by filtration and the filtrate was concentrated with a rotary evaporator under reduced pressure to afford a light yellow powder. Fractional recrystallization from 95% ethanol gave 0.026 g of N-xanthylidene-p-toluenesulfonamide m; 173-175° (lit.¹³ mp 167-168°); 0.659 g of 9-xanthione and 0.571 g of p-toluenesulfonimide.

Thermal Decomposition of 2. Compound 2 (0.20 g, 0.0007 mole) was placed into a small tube and slowly heated in an oil bath. When the bath temperature reached ca. 115° the sample began to darken. Melting occurred over a range from 126-134°. The sample melted to a dark red melt which then faded to a light yellow. When the bath temperature had reached 140°, the sample tube was removed and allowed to cool. The resulting mass was dissolved in hot anhydrous THF and filtered from an amorphous yellow solid which was identified as elemental sulfur. The filtrate, upon cooling, deposited 0.099 g (56%) of colorless needles which were subsequently identified as N-[bis(dimethyl)amino] methylene-p-toluenesulfonimide mp 140-143° (lit.¹⁴ m; 143-145°).

These same products were isolated when 2 was suspended in refluxing THF for 24 hours.

Hydrolysis of 3. Thione S-imide 3 (0.42 g, .0014 mole) was added to 15 ml of anhydrous methanol at 25° to afford a colorless solution. Upon addition of 3 ml of water an exothermic reaction occurred and the solution became intensely yellow and remained so for 5 minutes at which time the color faded. Evaporation of the solvent under reduced pressure gave 0.42 g of a 1:1 mixture of p-toluenesulfonimide and 1,3-dimethylimidazole-2-thione as established by nmr spectroscopy and thin layer chromatography (alumina, EtOAc/Et₂O 1:9). No other products could be detected.

~~Attempted Oxidation of 1,3-dimethylimidazole-2-thione.~~ (a) To a solution of 1,3-dimethylimidazole-2-thione (1.28 g, .01 mole) in 50 ml methylene chloride at 25° was added m-chloroperbenzoic acid (17.3 g, .1 mole) in small portions. After each addition a very exothermic reaction with gas evolution occurred. The solvent was evaporated under reduced pressure and the remaining solid washed with cold aqueous sodium bicarbonate. The resultant solid appeared to be the starting thione by nmr analysis. A small sample was recrystallized from hot water and proved to be 1,3-dimethylimidazole-2-thione by mixture melting point comparison. (b) 1,3-Dimethylimidazole-2-thione (2.56 g, .02 mole) was dissolved in 200 ml water and cooled to 5° to which addition of 4 ml 30% aqueous hydrogen peroxide (1.2 g, .035 mole) led to virorous gas evolution. Under reduced pressure the volume of the resultant solution was reduced to 50 ml, cooled to 5° and the crystalline precipitate which formed (2.5 g) was identified as starting thione.

~~Reaction of 3 with tetramethylthiourea.~~ To a solution of 3 (.297 g, .001 mole) in a minimum amount of CDCl_3 was added tetramethylthiourea (.132 g, .001 mole) in one portion. The reaction at 25° was followed by nmr spectroscopy and after 24 hours indicated the complete conversion of 3 to 2 and 1,3-dimethylimidazole-2-thione, without the formation of any other products. Evaporation of the solvent and crystallization of the residual solid from anhydrous methanol gave .12 g of 2.

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